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(54) Green light emitting phosphors

(57) A green light emitting phosphor suitable for a phosphor screen of a cathode ray tube used as a projecting tube of a projection television receiver is represented by a general formula $Y_3Al_xGa_{5-x}O_{12}$:Tb. The most preferred composition is $Y_3Al_2Ga_3O_{12}$:Tb wherein the Tb density or the molar percentage of Tb/(Y + Tb) is equal to 5 mol %.

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FIG.1

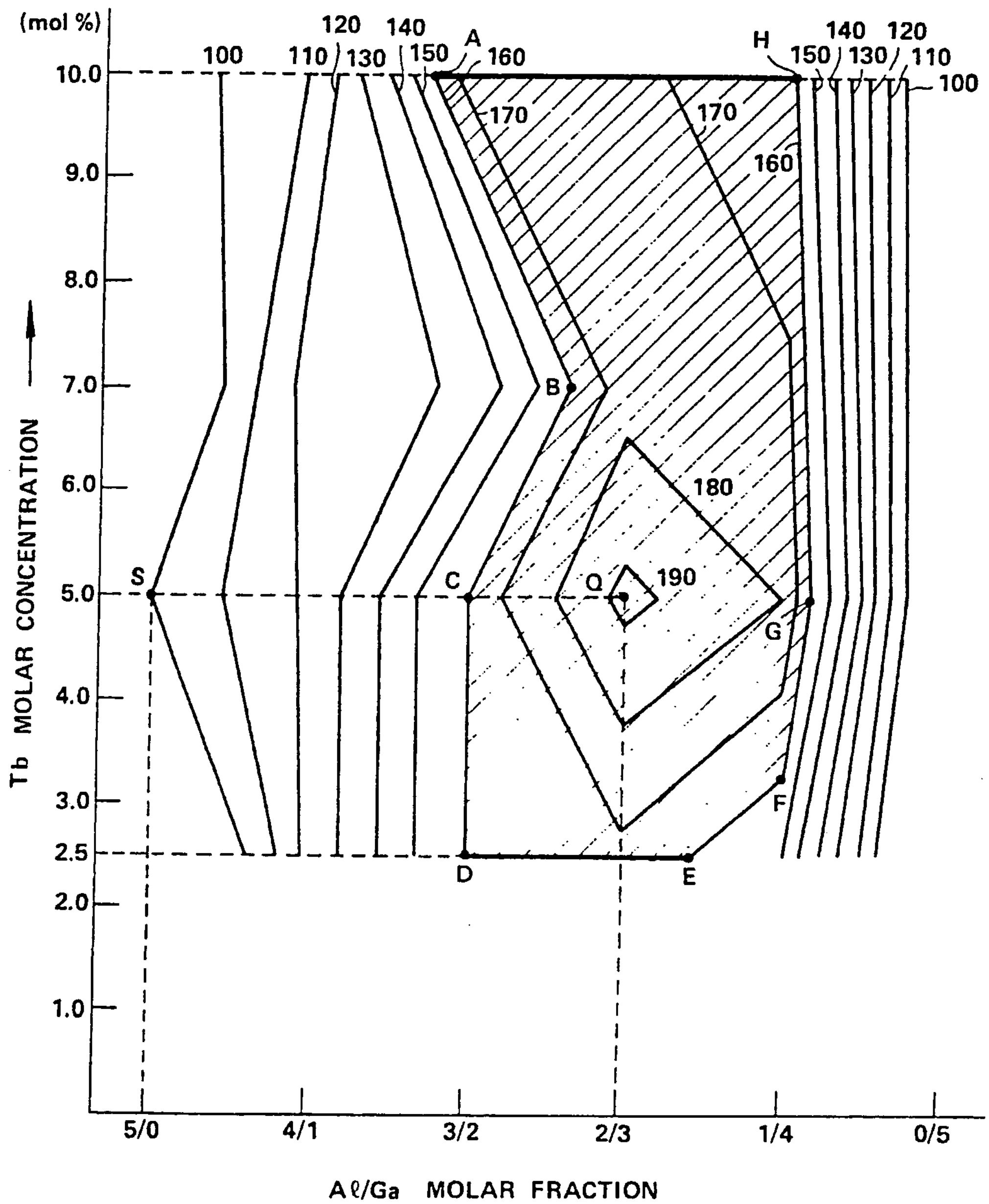

(mol %)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.5
2.0
1.0
Tb MOLAR CONCENTRATION
5/0
4/1
3/2
2/3
1/4
0/5
Aℓ/Ga MOLAR FRACTION
100
110
120
130
140
150
160
170
180
190
A
B
C
D
E
F
G
H
Q
S

FIG.2

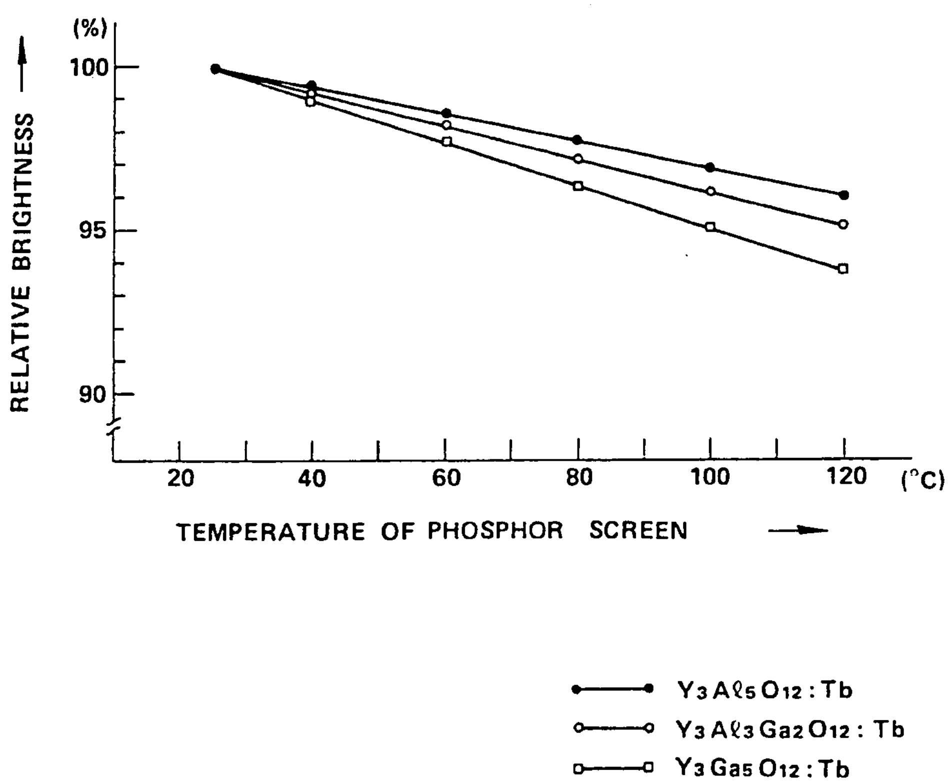
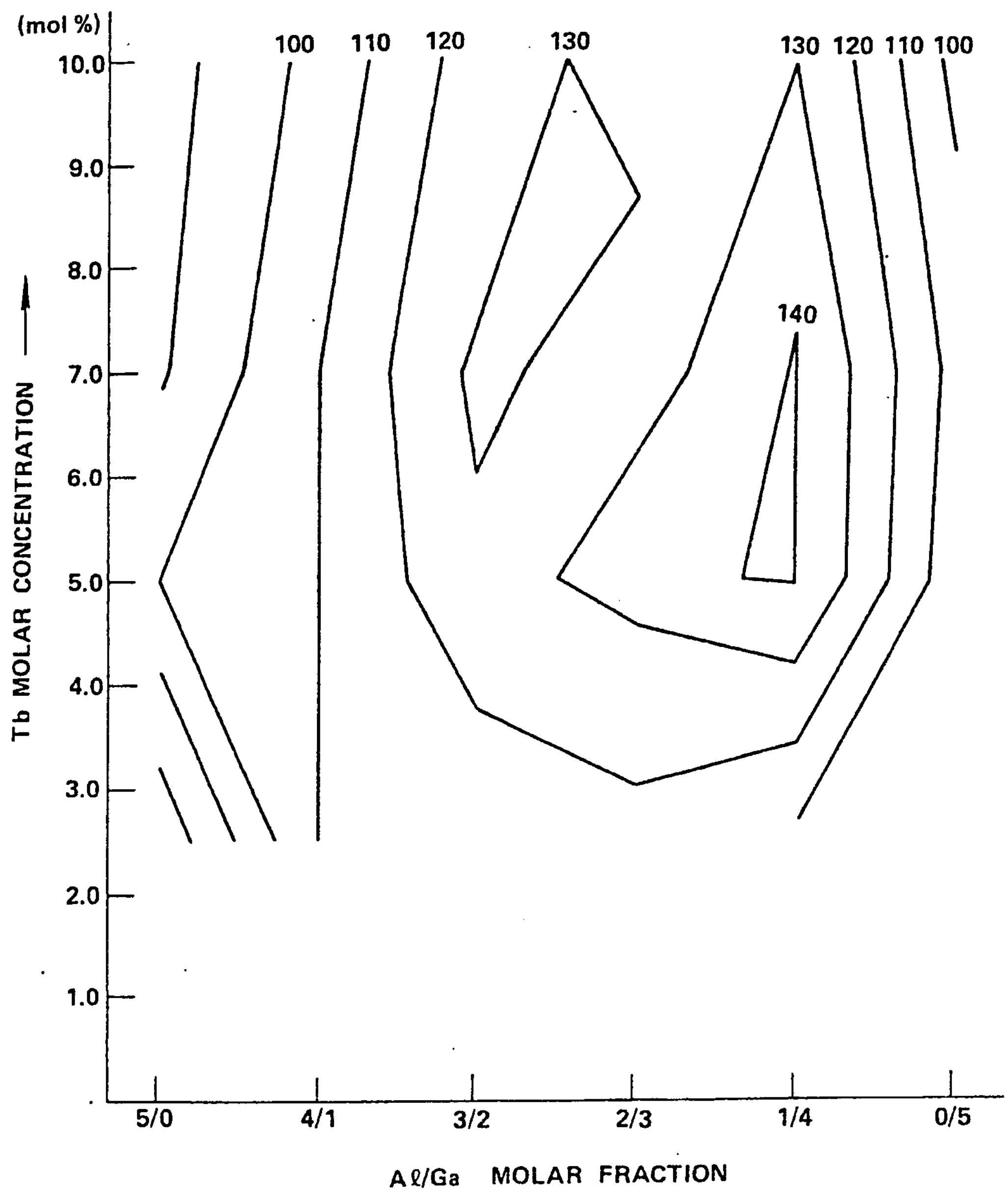
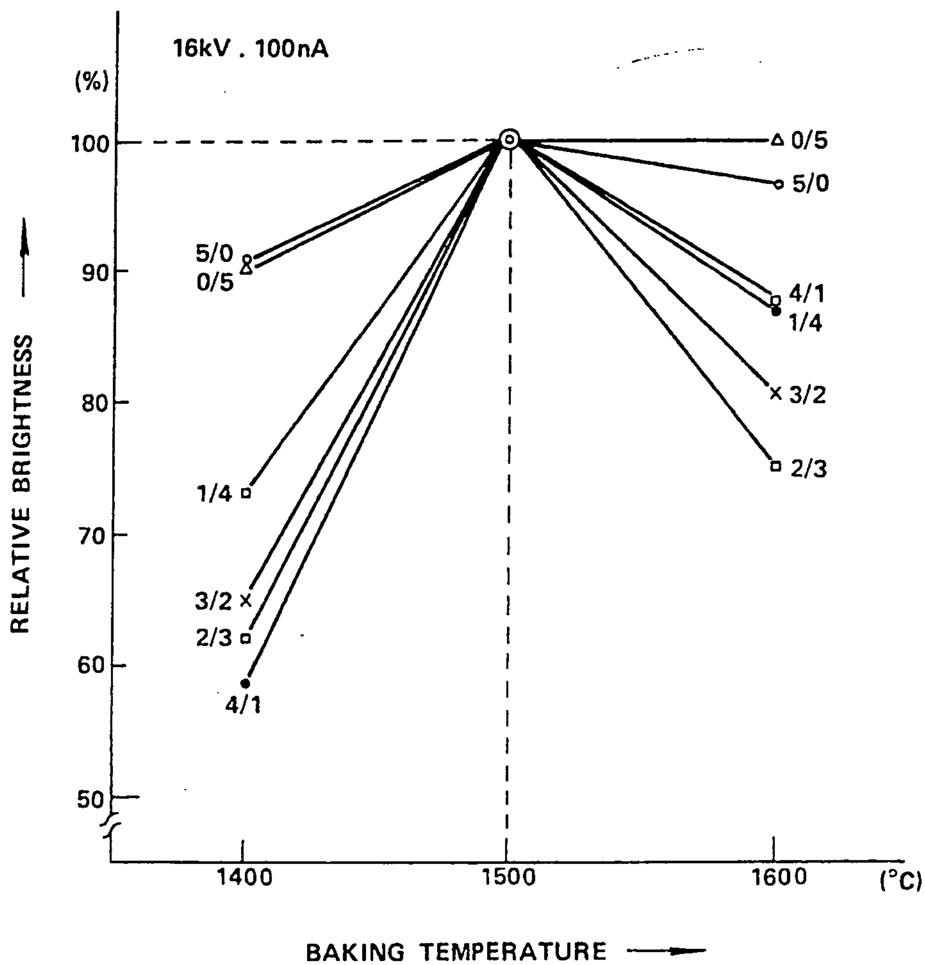

(%)
100
95
90
RELATIVE BRIGHTNESS
20
40
60
80
100
120
(°C)
TEMPERATURE OF PHOSPHOR SCREEN
$Y_3Al_5O_{12}:Tb$
$Y_3Al_3Ga_2O_{12}:Tb$
$Y_3Ga_5O_{12}:Tb$

FIG.3



(mol %)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
Tb MOLAR CONCENTRATION
100
110
120
130
130
120
110
100
140
5/0
4/1
3/2
2/3
1/4
0/5
Aℓ/Ga MOLAR FRACTION

FIG.4


16kV . 100nA
(%)
100
90
80
70
60
50
RELATIVE BRIGHTNESS
0/5
5/0
4/1
1/4
3/2
2/3
5/0
0/5
1/4
3/2
2/3
4/1
1400
1500
1600
(°C)
BAKING TEMPERATURE

SPECIFICATION

Green light emitting phosphors

This invention relates to green light emitting phosphors. More particularly, but not exclusively, the invention relates to green light emitting phosphors suitable for use in a so-called projection type television receiver. The invention also relates to cathode ray tubes having a screen incorporating such a green light emitting phosphor.

In general, the phosphor applied to the phosphor screen of a cathode ray tube (CRT) of a projection television receiver is required to emit light of extremely high brightness when excited. As the green phosphor, the composition Gd_2O_2S:Tb has been used. However, this phosphor has inferior thermal quenching and current-brightness saturation characteristics. More recently, therefore, the phosphor composition $Y_3Al_5O_{12}$:Tb has been preferred because dissymmetry between the three primary colours (that is, loss of so-called white balance) due to thermal quenching can be eliminated, and the phosphor shows higher brightness, so is usable in a projection television receiver. However, for increasing the brightness of the projected image on the projection television receiver, it has become necessary to cause the phosphor to emit the light of still higher brightness by exciting the phosphor more strongly by using, for example, a multi-beam electron gun capable of increasing the beam current by several times to some tens of times by using several electron beams. In such a case, however, the $Y_3Al_5O_{12}$:Tb phosphor exhibits some brightness saturation. Thus, with the currently employed projection type CRT, the current or electron density is approximately 5 to 20 $\mu A/cm^2$, at which the aforementioned composition $Y_3Al_5O_{12}$:Tb used as the green phosphor is still free from brightness saturation. However, this is not the case when the beam current (cathode current) is increased further, so that the current density is equal to 20 to 80 $\mu A/cm^2$ or even to 100 $\mu A/cm^2$, whereupon the phosphor becomes subject to brightness saturation. For this reason, a demand has arisen for a green phosphor which is free from brightness saturation and capable of exhibiting stabilized light emitting characteristics under conditions of a stronger excitation.

The composition $Y_3Al_xGa_{5-x}O_{12}$:Tb corresponding to the aforementioned composition wherein some Al is replaced by Ga, exhibits brightness saturation characteristics that are superior to those of the composition $Y_3Al_5O_{12}$:Tb. However, this composition has the drawback that difficulties are encountered in baking or calcining the material for producing the single phase material, and that considerable time and labour are involved in obtaining the material in powder form, because the phosphor tends to solidify upon baking. In addition, it has been shown that the phosphor may undergo considerable fluctuations in brightness characteristics when fluctuations occur in the baking temperature.

According to the present invention there is provided a phosphor material having a composition of $Y_3Al_xGa_{5-x}O_{12}$:Tb wherein the Al/Ga molar ratio and Tb/(Y + Tb) molar percentage when plotted in a rectangular coordinate system are included within an area defined by a closed loop obtained by connecting points A to H which represent the following values of said molar ratio and said molar percentage, respectively:

A	3.3/1.7,	10.0 mol %
B	2.4/2.6,	7.0 mol %
C	3.0/2.0,	5.0 mol %
D	3.0/2.0,	2.5 mol %
E	1.6/3.4,	2.5 mol %
F	1.0/4.0,	3.2 mol %
G	0.9/4.1,	5.0 mol %
H	1.0/4.0,	10.0 mol %

The baking step of the manufacture process of the phosphor material is preferably carried out at 1500°C for obtaining the maximum brightness level.

It is possible with the green phosphor meeting the above conditions to obtain a brightness level about 60 to 90% higher than with the conventional $Y_3Al_5O_{12}$:Tb composition under conditions of stronger excitation, for example, at a current density of 90 $\mu A/cm^2$, the phosphor being still free from brightness saturation. In addition, the starting composition can be formulated easily, and the finished phosphor material exhibits stable light emitting characteristics with little fluctuation in the brightness level caused by changes in the composition.

The invention will now be described by way of example with reference to the accompanying drawings, in which:

Figure 1 is a graphic chart in which the relative brightness for an excitation voltage of 30 kV and a current density of 90 $\mu A/cm^2$ is plotted with contour lines;

Figure 2 is a graphic chart in which relative brightness is plotted against increase in the phosphor screen temperature;

Figure 3 is a graphic chart in which the relative brightness for an excitation current of 30 kV and a current density of 10 $\mu A/cm^2$ is plotted with contour lines; and

Figure 4 is a graphic chart in which are shown the changes in relative brightness related to the baking temperature employed during the preparation of the phosphor.

The preferred embodiment of green light emitting phosphor for a colour television projector and according to the present invention, is a phosphor having the composition Y_3Al-

$_2Ga_3O_{12}$:Tb, wherein the molar fraction Al/Ga is equal to 2/3 and the molar percentage Tb/(Y + Tb) is equal to 5 mol %. The method of producing the phosphor will now be explained.

Example

A powder mixture having the composition:

Y_2O_3	(purity, 4N)	32.18 g
Al_2O_3	(purity, 4N)	10.20 g
Ga_2O_3	(purity, 4N)	28.12 g
Tb_4O_7	(purity, 4N)	2.80 g

(wherein purity 4N represents a purity of 99.99% or four-nine purity)

is prepared as the starting material necessary for producing the above composition $Y_3Al_2Ga_3O_{12}$:Tb (where the Tb density or concentration is equal to 5 mol %). To this mixture is added 3.51 g of BaF_2 as flux (reagent of a special grade) and the resulting mixture is dissolved in 70 cc of ethanol as a solvent and is ground in a ball mill. Thus the mixture is charged into an alumina vessel together with alumina balls about 5 mm in diameter and higher than about 99.8% in purity, and ground for about 15 hours at 30 to 100 rpm, for example, 30 rpm. The alumina balls are used in a weight twice or three times that of the starting mixture. The ball-milled starting mixture is filtered or otherwise separated from the alumina balls, dried and freed of ethanol.

The ball-milled and dried materials are charged into a capped alumina crucible of high purity (for example, higher than 99.8%) and the cap and the main body of the crucible are sealed together with a heat-resistance adhesive such as "aron-ceramic D" manufactured and sold by the Toagosei Chemical Industry Co., Ltd.

The crucible is charged into a furnace and heated to a temperature of 1500°C at a rate of 200°C per hour. It is then kept at this temperature for 2 hours for baking and allowed to cool in the furnace.

Then, for removing the residual flux from the thus baked phosphor material, it is rinsed in an agitator for 30 to 60 minutes with 1.5N nitric acid which is used at the rate of 10 cc per gram of phosphor.

The phosphor $Y_3Al_2Ga_3O_{12}$:Tb obtained in the above described manner (with a Tb density or concentration of 5 mol %) was used in the preparation of a CRT for a colour television projector (projector tube) and its brightness and temperature characteristics were measured.

In a similar manner, various samples of $Y_3Al_xGa_{5-x}O_{12}$:Tb phosphor with the molar fraction Al/Ga in the range from 5/0 to 0/5 and the molar percentage Tb/(Y + Tb) in the range from 2.5 to 10.0 mol %, were prepared and used in the projector tube, and the brightness and temperature characteristics of these various samples were also measured.

Fig. 1 shows the relative brightness of the phosphor $Y_3Al_5O_{12}$:Tb (with a Tb density or concentration of 5 mol %), with the reference brightness being 100, the exciting voltage of the associated projection tubes being 30 kV, and the cathode current Ik for the raster size of 100 cm^2 being 9.0 mA (with the current density being 90 $\mu A/cm^2$). In the graphic chart shown in Fig. 1, the Al/Ga molar ratio is plotted on the abscissa and the Tb density or concentration or mol % of Tb/(Y + Tb) is plotted on the ordinate. In this graphic chart, a point S represents the $Y_3Al_5O_{12}$:Tb which gives the aforementioned brightness reference with the Tb density or concentration being 5 mol %. The solid broken lines in the chart represent equi-brightness lines connecting the points of equal relative brightness in the same manner as the contour lines. The numeral affixed to each broken line designates the relative brightness corrected for the luminosity factor.

It is seen from this figure that the relative brightness is changed from 100 to a higher level of 190 although the exciting condition (voltage of 30 kV and current density of 90 $\mu A/cm^2$) remains the same. It is at a point Q with the Al/Ga ratio being 2/3 (the phosphor composition thus being $Y_3Al_2Ga_3O_{12}$:Tb) and the Tb density or concentration being at or near 5 mol %, that the value of the relative brightness reaches a maximum of 190 which is most preferred as the phosphor for the television projector. It is in the area shown by hatching in the Al/Ga ratio-Tb density coordinate system and having a relative brightness level which is higher than 160 that the phosphor may safely be used in the television projector. The aforementioned area with the relative brightness higher than 160 and with the pitch of the equi-brightness lines becoming larger is preferred because, in the area of denser equi-brightness lines, for example, in the area with the Al/Ga ratio in the range of 1/4 to 0/5, the slightest change in the Al/Ga ratio causes drastic changes in brightness so that the starting material would have to be formulated with the utmost accuracy, and difficulties would be presented in obtaining uniform brightness. For this reason, the area in the chart with the relative brightness higher than 160 and with larger equi-brightness line intervals from one another in the drawing is preferred.

A Tb density or concentration lower than 2.5 mol % is also not preferred because then the light emitted by the phosphor would be more diluted with white and would not be balanced with the red and blue light, so there would be loss of white balance. With the Tb density or concentration higher than 10 mol %, it is impossible to elevate the value of relative brightness further. Moreover, terbium (Tb) is expensive and therefore it would be

impractical to use the material in more than the required amounts because of the increased manufacturing costs. In addition, the value of relative brightness reaches its maximum at or near the Tb density or concentration of 5.0 mol %. For this reason the upper limit for the Tb density or concentration has been selected to be 10.0 mol %.

To summarize, the phosphor with the composition $Y_3Al_xGa_{5-x}O_{12}$:Tb whose Al/Ga ratio and Tb density or concentration are included within an octagon defined by connecting the points A to H in the chart of Fig. 1, excluding the boundary line, is most suitable as the phosphor for a television projector. The Al/Ga ratio and Tb density or concentration or Tb/(Y + Tb) molar percentage for the points A to H are given in the Table below.

TABLE

	Al/Ga molar ratio	Tb density (mol %)
A	3.3/1.7	10.0
B	2.4/2.6	7.0
C	3.0/2.0	5.0
D	3.0/2.0	2.5
E	1.6/3.4	2.5
F	1.0/4.0	3.2
G	0.9/4.1	5.0
H	1.0/4.0	10.0

In particular, the area centred about a point Q in Fig. 1 with the Al/Ga ratio of 2/3 and the Tb density or concentration of 5.0 mol %, and showing only gentle changes in brightness, and hence the phosphor with, for example, a composition $Y_3Al_xGa_{5-x}O_{12}$:Tb with the Al/Ga ratio in the range of 2.5/2.5 to 1.5/3.5 and with the Tb density in the range of 3.5 to 10.0 mol %, are most preferred.

Under conditions of stronger excitation such as 30 kV for electrical voltage and 90 $\mu A/cm^2$ for current density, the CRT phosphor screen of the green phosphors for the television projector reaches the temperature of 80 to 100°C even when the screen is cooled by liquid cooling as currently employed for a television projector. Thus it becomes necessary to consider the problem of thermal quenching. Referring to Fig. 2, there are shown changes in relative brightness caused by the increased phosphor screen temperature. Thus the relative brightness of three different kinds of phosphor, namely $Y_3Al_5O_{12}$:Tb, $Y_3Al_3Ga_2O_{12}$:Tb and $Y_3Ga_5O_{12}$:Tb are shown with the brightness value for the phosphor screen temperature of 25°C being 100% for these three phosphors. It is seen from this figure that, while the relative brightness of these phosphors is lowered gradually with increase in the phosphor screen temperature, the amount of decrease in the relative brightness is not higher than 3.0 to 5.0%, which is acceptable in practice.

In Fig. 3, the values of relative brightness are plotted in a coordinate system of Al/Ga ratio-Tb density for the excitation voltage of 30 kV and the cathode current of 1.0 mA, and thus for the current density of 10 $\mu A/cm^2$ with a raster size of 100 cm^2. The various values of relative brightness of the phosphor samples are plotted by equi-brightness lines with the brightness for the $Y_3Al_5O_{12}$:Tb under the same exciting conditions being used as reference brightness (100). It is seen from this figure that the area with the relative brightness higher than 120 and especially higher than 130 or 140 is generally coincident with the area of relative brightness higher than 160 for the aforementioned stronger state of excitation shown in Fig. 1 (with the electrical voltage of 30 kV and the current density of 90 $\mu A/cm^2$).

Fig. 4 shows relative brightness of several samples of green phosphors for baking temperatures of 1400°C, 1500°C and 1600°C employed at the time of manufacture of the phosphor samples, with the relative brightness for the baking temperature of 1500°C being used as reference brightness (100%). In this figure, the relative brightness is shown of the six phosphor samples with the molar ratio of Al/Ga in the composition of $Y_3Al_xGa_{5-x}O_{12}$:Tb being 0/5, 1/4, 2/3, 3/2, 4/1 and 5/0. It is seen from the figure that the brightness becomes a maximum with the baking temperature of 1500°C for the samples except the one with the Al/Ga molar ratio equal to 0/5. Thus it is preferred that, in the manufacture of the green phosphor, the baking temperature of 1500°C be employed and the rate of temperature elevation or retention time at the baking temperature be also selected as set forth in the above Example.

In addition, as disclosed in our copending Patent Application No. 8227684 (serial No. 2 106 924) it is preferred that, immediately after baking, the phosphor be freed of residual flux (BaF_2) by washing with an acid or alkali in order to avoid "burning" of the phosphor.

It is to be noted that the present invention is not limited to the above described embodiments, but may comprise various modifications. For example, $BaCl_2$ or a mixture thereof with BaF_2 may be used as the flux for the preparation of the phosphor. These fluxes may be used in any suitable amount different from the value given in the above Example. In addition, an aqueous solution of sodium hydroxide or hydrochloric acid may be employed in place of nitric acid for washing the baked phosphor for removing the residual solvent.

It is seen from the foregoing that the embodiment of green phosphor for a television projector and according to the present invention is free of brightness saturation and sub-

ject to only negligible thermal quenching even when the current density in the projector tube or CRT is increased to 20 $\mu A/cm^2$ to 80 $\mu A/cm^2$ or even to 100 $\mu A/cm^2$. Thus a projection CRT with extremely high brightness can be realized with the use of a multi-beam electron gun. Moreover, the phosphor is not affected in brightness by small fluctuations in the mixture ratio of the starting composition. In addition, the phosphor is simple to manufacture and exhibits stable light emitting characteristics.

CLAIMS

1. A phosphor material having a composition of $Y_3Al_xGa_{5-x}O_{12}$:Tb wherein the Al/Ga molar ratio and Tb/(Y + Tb) molar percentage when plotted in a rectangular coordinate system are included within an area defined by a closed loop obtained by connecting points A to H which represent the following values of said molar ratio and said molar percentage, respectively:

A	3.3/1.7,	10.0 mol %
B	2.4/2.6,	7.0 mol %
C	3.0/2.0,	5.0 mol %
D	3.0/2.0,	2.5 mol %
E	1.6/3.4,	2.5 mol %
F	1.0/4.0,	3.2 mol %
G	0.9/4.1,	5.0 mol %
H	1.0/4.0,	10.0 mol %.

2. A phosphor material according to claim 1 wherein said phosphor material is baked at a temperature of 1500°C at the time of manufacture.

3. A phosphor material according to claim 2 wherein said phosphor material is heated to said temperature of 1500°C at the rate of 200°C per hour and kept at the temperature for two hours for baking.

4. A phosphor material substantially as hereinbefore described with reference to the Example.

5. A cathode ray tube having a screen incorporating a phosphor material according to any one of the preceding claims.

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